

Electronic Supplementary Information for MS:

**An unprecedented 3-fold interpenetrated double-edged
pseudo-diamondoid network containing exceptional 5-fold
interlocking tri-flexure helices and 15-fold interwoven helices**

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Experimental Section

Materials and general methods. All chemicals were commercially purchased and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. Cd was determined by a tps-7000 Plasma-Spec(I) inductively coupled plasma atomic emission spectrometer (ICP-AES). IR spectrum was recorded in the range 400-4000 cm^{-1} on a Bio-Rad FTS-185 FT/IR Spectrophotometer using KBr pellets. TG analysis was performed on a NETZSCH STA 449C instrument in flowing N_2 with a heating rate of 10 $^\circ\text{C}\cdot\text{min}^{-1}$. Excitation and emission spectra were performed on an F-4500 fluorescence spectrophotometer equipped with a 150 W xenon lamp as the excitation source. XRPD data were recorded on a XD-3 diffractometer using Cu $K\alpha$ radiation.

Synthesis of $[\text{Cd}_3(\text{ppa})_2(\text{oba})_2(\text{H}_2\text{O})_3]\cdot 0.25\text{H}_2\text{O}$ (1). A mixture of $\text{Cd}(\text{OAc})_2\cdot 2\text{H}_2\text{O}$ (0.160g, 0.6 mmol), pipemidic acid (0.091g, 0.3 mmol), H_2oba (0.077g, 0.3 mmol), KOH (0.15 mL, 2.5 M) and distilled water (8 mL) was stirred for 10 min in air, then transferred and sealed in an 18 mL Teflon-lined autoclave, which was heated at 135 $^\circ\text{C}$ for 72 h. After naturally cooling to the room temperature, colorless block crystals of **1** were filtered off, washed with distilled water, and dried at ambient temperature (yield: 57% based on H_2oba). Elemental analysis (%) calcd for $\text{C}_{56}\text{H}_{58.50}\text{Cd}_3\text{N}_{10}\text{O}_{19.25}$ (1516.83): C 44.34; H 3.89; N 9.23; Cd 22.23; found: C 44.12; H 3.71; N 9.44; Cd 22.46%. IR (KBr, cm^{-1}): 3406(m), 3243(m), 2981(w), 2932(w), 2261(w), 1916(w), 1635(s), 1606(s), 1560(s), 1505(m), 1474(m), 1452(m), 1432(m), 1365(s), 1314(m), 1251(m), 1232(s), 1161(s), 1126(m), 1016(m), 962(w), 919(w), 876(m), 844(w),

819(m), 782(w), 763(m), 713(w), 648(w), 618(w), 568(w), 545(w), 506(w), 452(w),
425(w).

Crystallographic Data Collection and Refinement

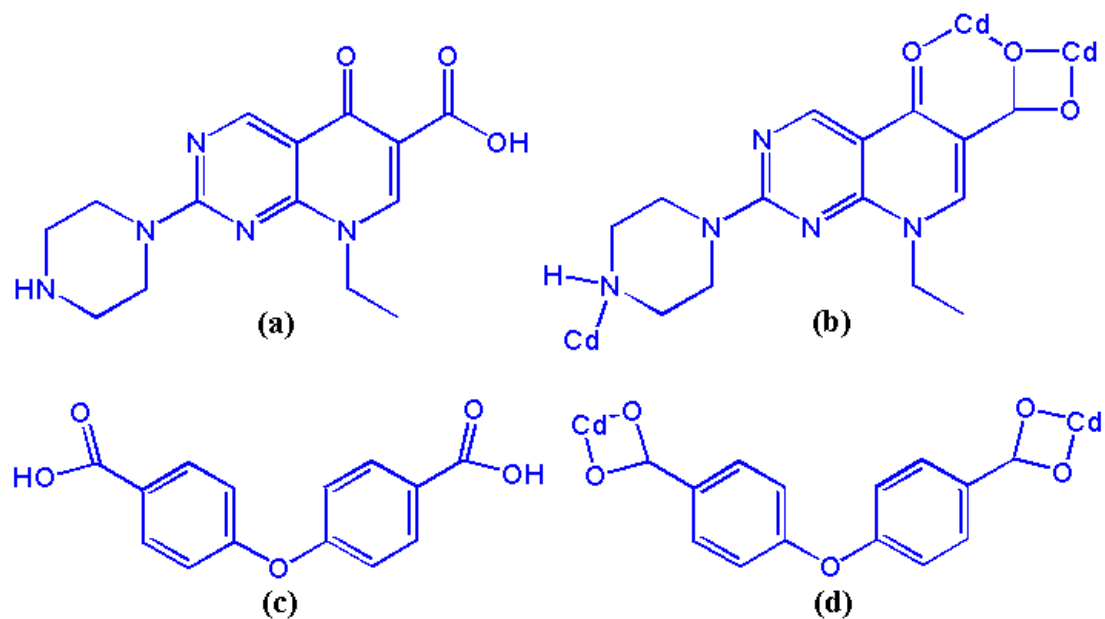
Single-crystal X-ray diffraction data for compound **1** were collected on a Bruker Smart Apex CCD diffractometer with Mo K α monochromated radiation ($\lambda = 0.71073 \text{ \AA}$) at 296(2) K. Empirical absorption correction was applied using the multi-scan technique. The structure of **1** was solved by the direct method and refined by the full-matrix least-squares on F^2 using the SHELXL-97 software.¹ All of the non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were generated geometrically. The aqua hydrogen atoms were located from difference Fourier maps.

CCDC 808119 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

Reference

- 1 (a) G. M. Sheldrick, *SHELXS 97, Program for Crystal Structure Solution*, University of Göttingen, Germany, 1997; (b) G. M. Sheldrick, *SHELXL 97, Program for Crystal Structure Refinement*, University of Göttingen, Germany, 1997.

Supporting Figures



Scheme S1 The molecular structures of ppaH (a) and H₂oba (c), and the coordination modes of ppa (b) and oba (d) ligands in **1**.

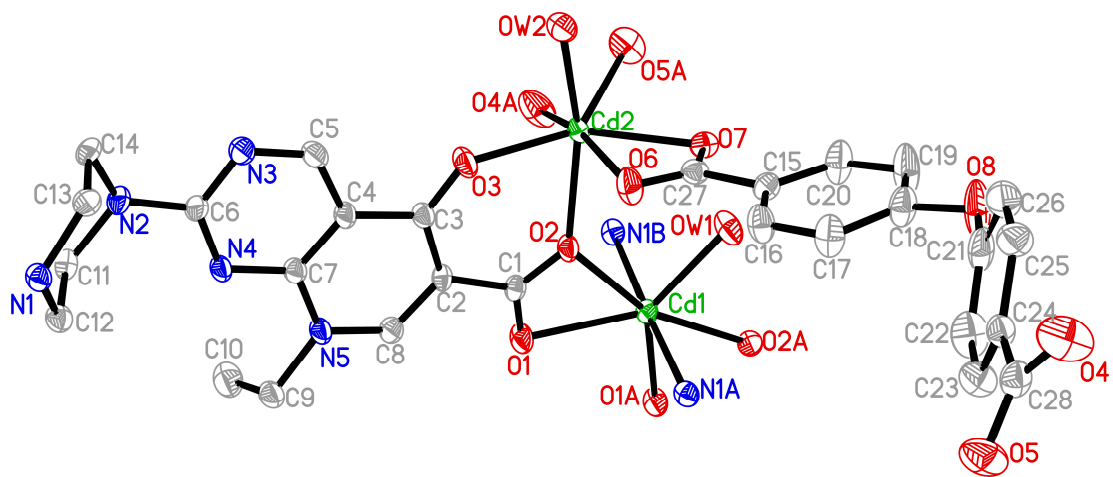


Fig. S1 ORTEP diagram showing the coordination environment for the Cd atoms in **1**.

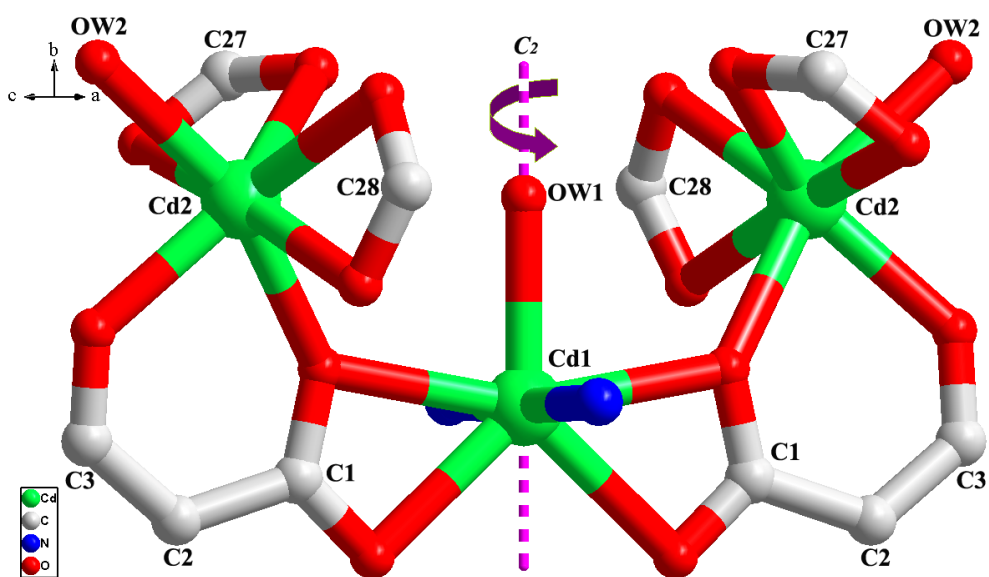


Fig. S2 Schematic representation of the trinuclear cadmium cluster

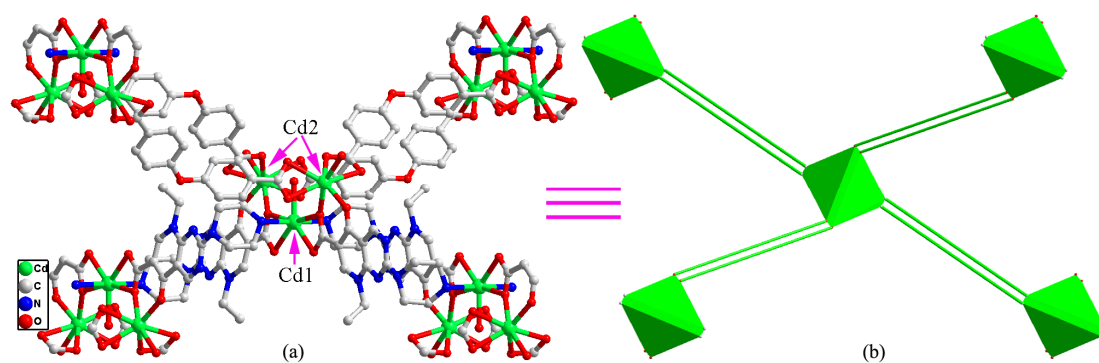


Fig. S3 Perspective (a) and simplified (b) views of the linkages of a trinuclear cadmium cluster with four adjacent clusters. Four “double-bridges” serve as four double-edged linkers.

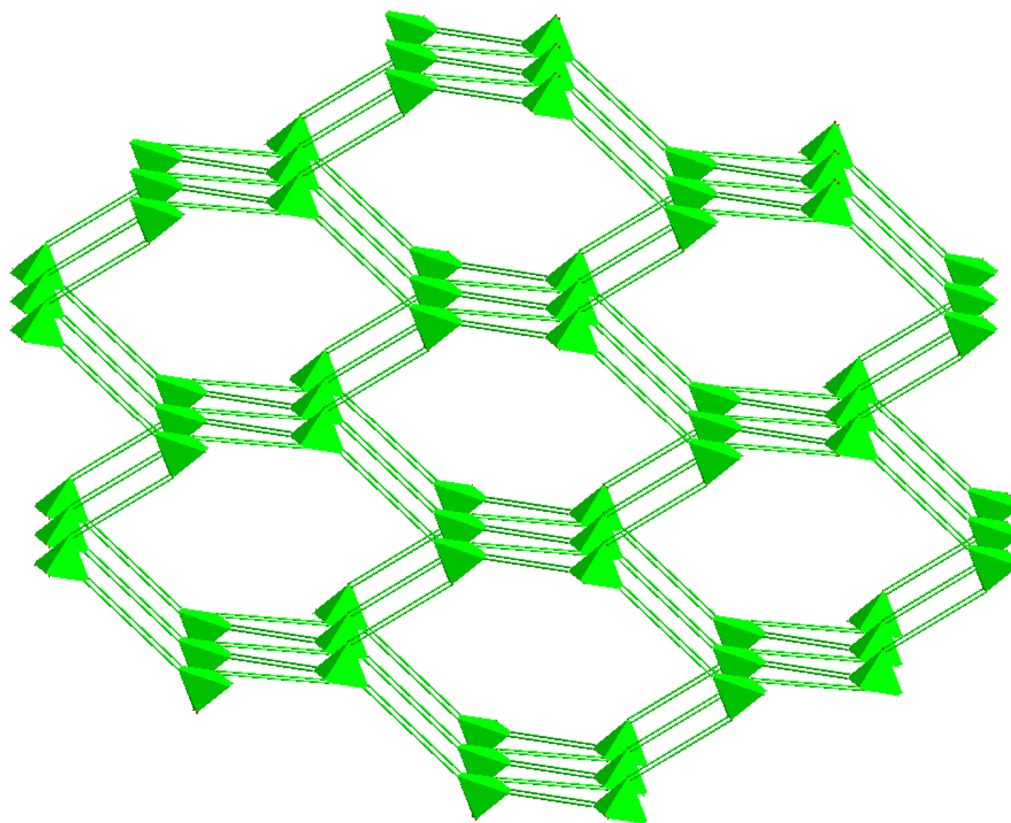


Fig. S4 A schematic representation of the single *pseudo-dia* network with double edges.

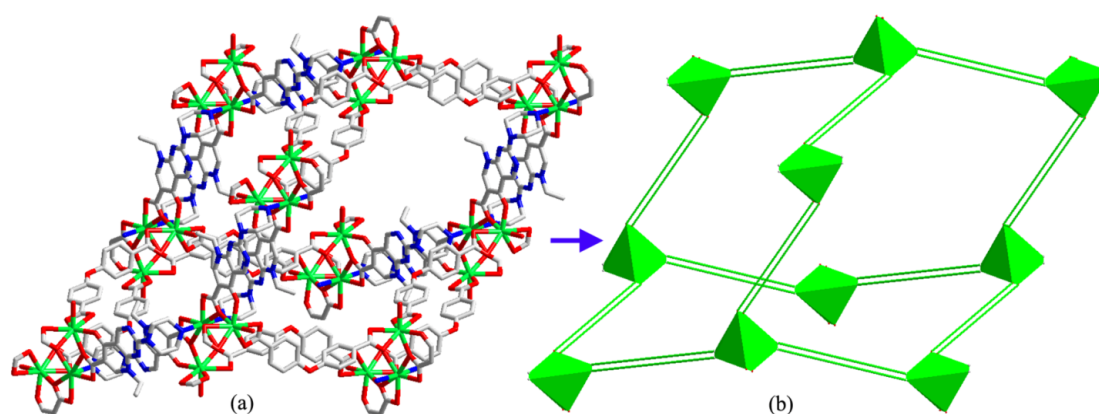


Fig. S5 Perspective (a) and schematic (b) views of the single adamantanoid cage with maximum dimensions of $48.42 \times 35.64 \times 29.02 \text{ \AA}$.

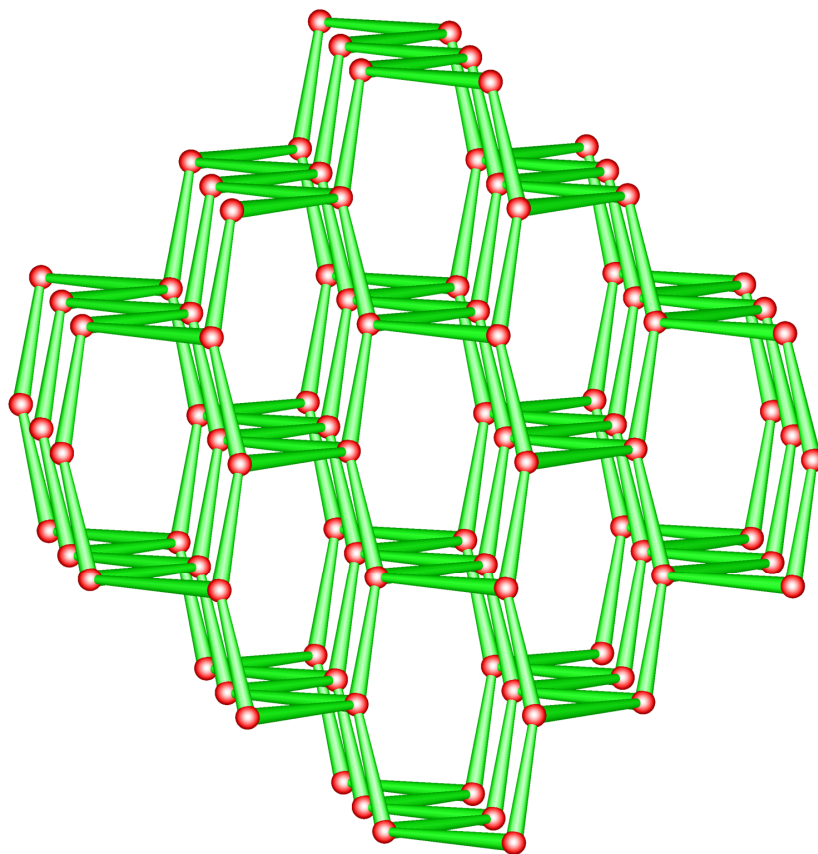


Fig. S6 Schematic representation of the ordinary **dia** net.

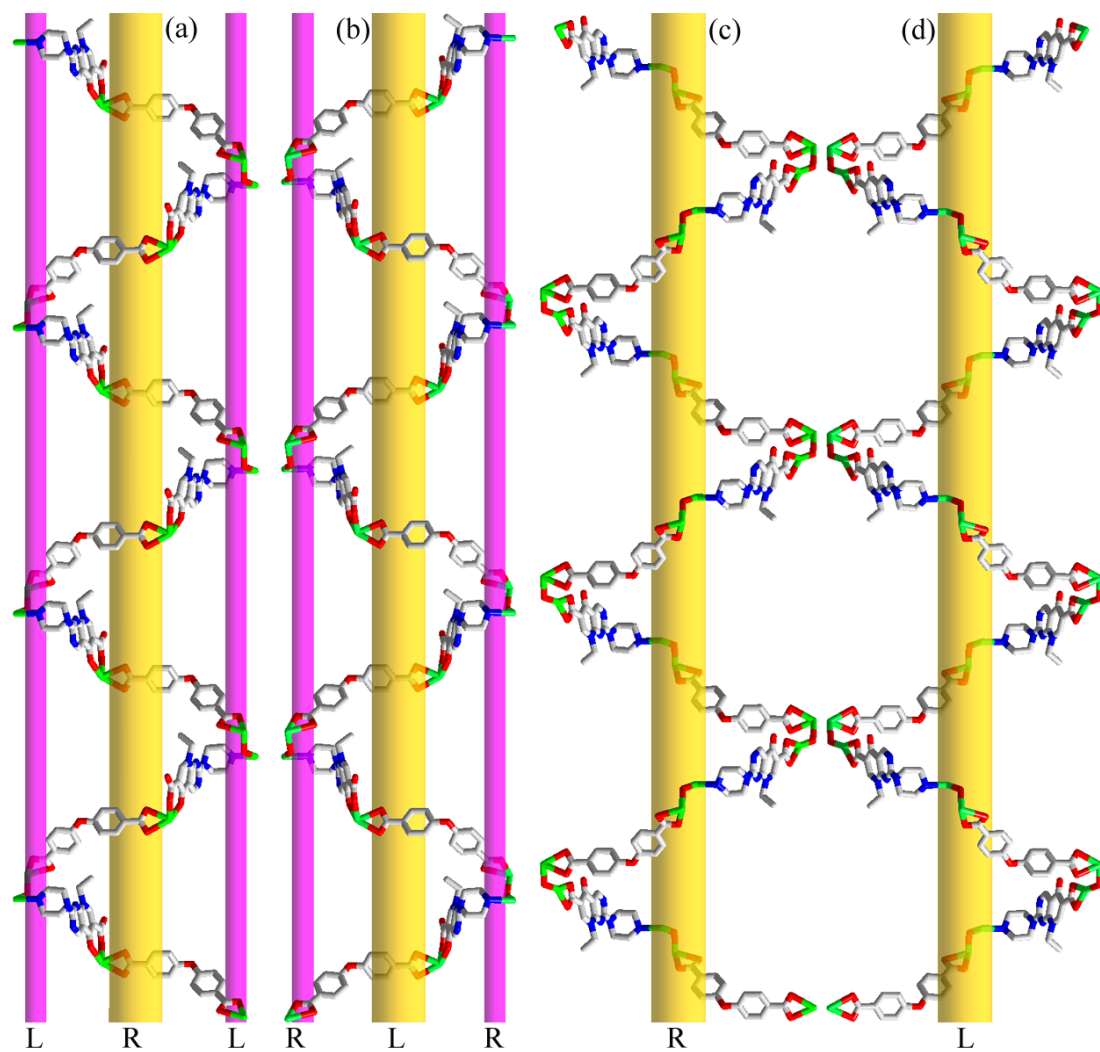


Fig. S7 Perspective views of two types tri-flexural helices with opposite chirality (a, b), and the left- and right-handed ordinary helices (c, d) of **1**.

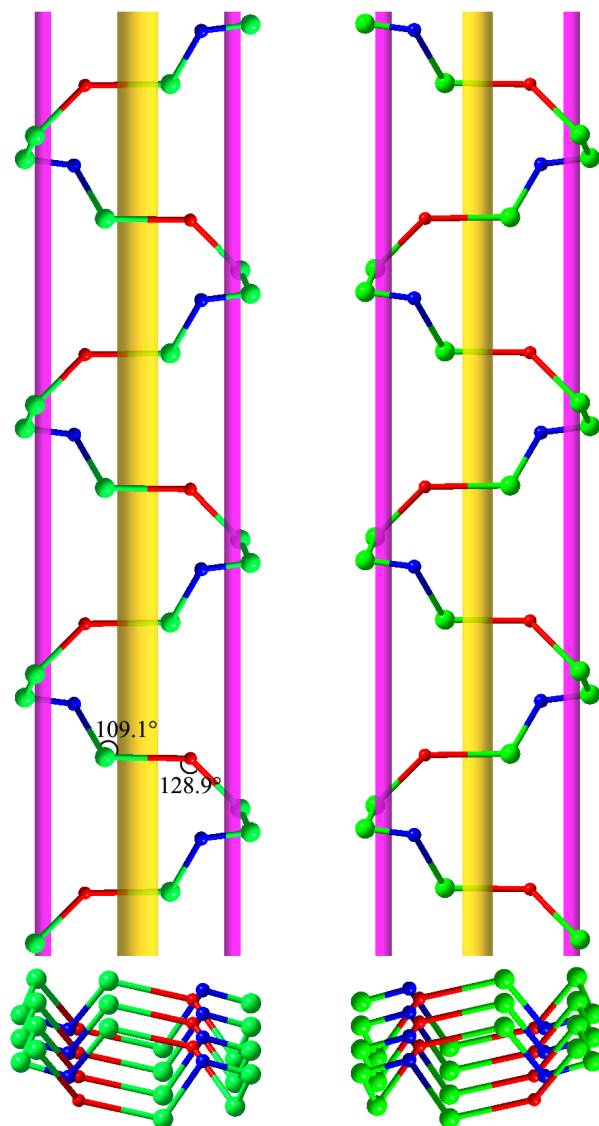


Fig. S8 Simplified views of two types tri-flexural helices with opposite chirality
(color code: Cd green, O red, N blue).

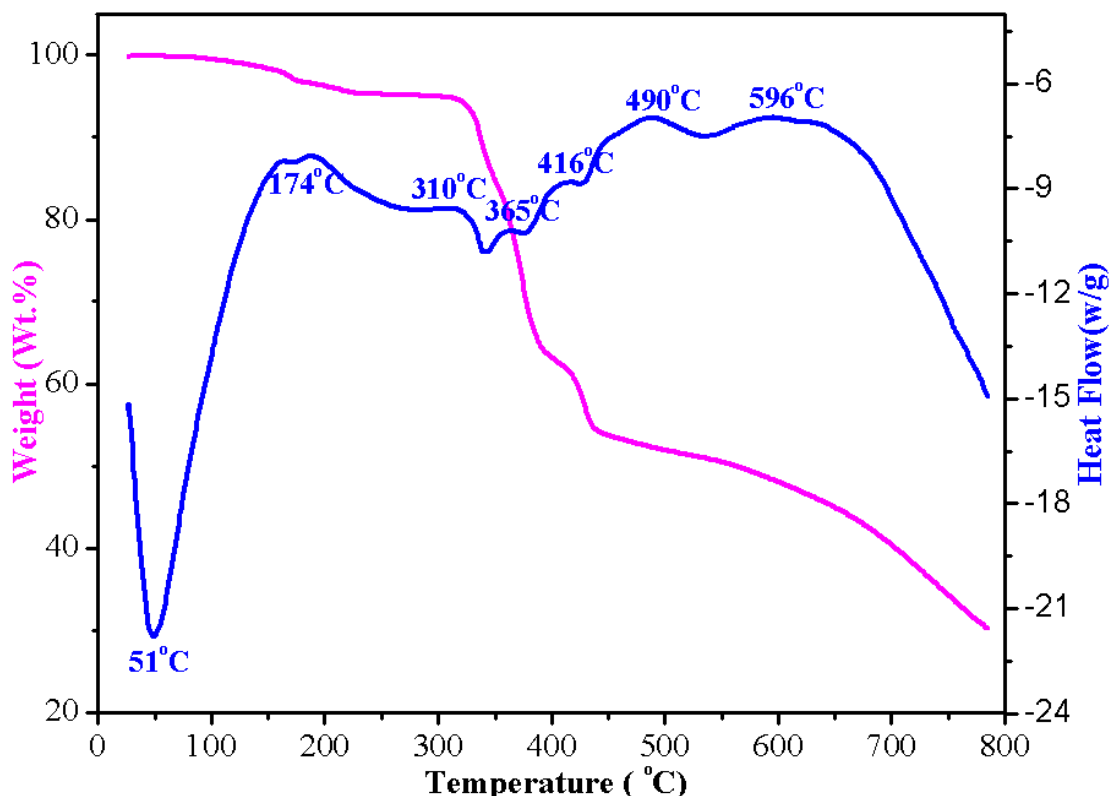


Fig. S9 The TG-DSC curves of compound **1**.

The thermogravimetric analysis (TG) curve of **1** exhibits three main weight losses (Fig. S9). The first weight loss is 4.50% in the temperature range of 50-225 °C, which corresponds to the release of the non-coordinated and coordinated water molecules (calcd 3.59%). The second weight loss of 34.19% at 305-420 °C corresponds to the release of the oba ligands (calcd 33.75%). The last weight loss starts from 420 °C and continues up to 800 °C, which corresponds to the further decomposing of the compound. The total weight loss of 69.78% is less than the calculated value of 74.60% if the final product is assumed to be CdO; hence, the decomposing process is not complete due to the use of N₂ atmosphere. In the DSC curve of **1**, the endothermic peak at 51 and 174 °C corresponds to the release of lattice and coordinated water molecules in **1**. The exothermic peaks at 310, 365 and 416 °C are attributed to the decomposition of the oba ligand. The exothermic peaks at 490 and 596 °C are attributed to the decomposition of the ppa ligand.

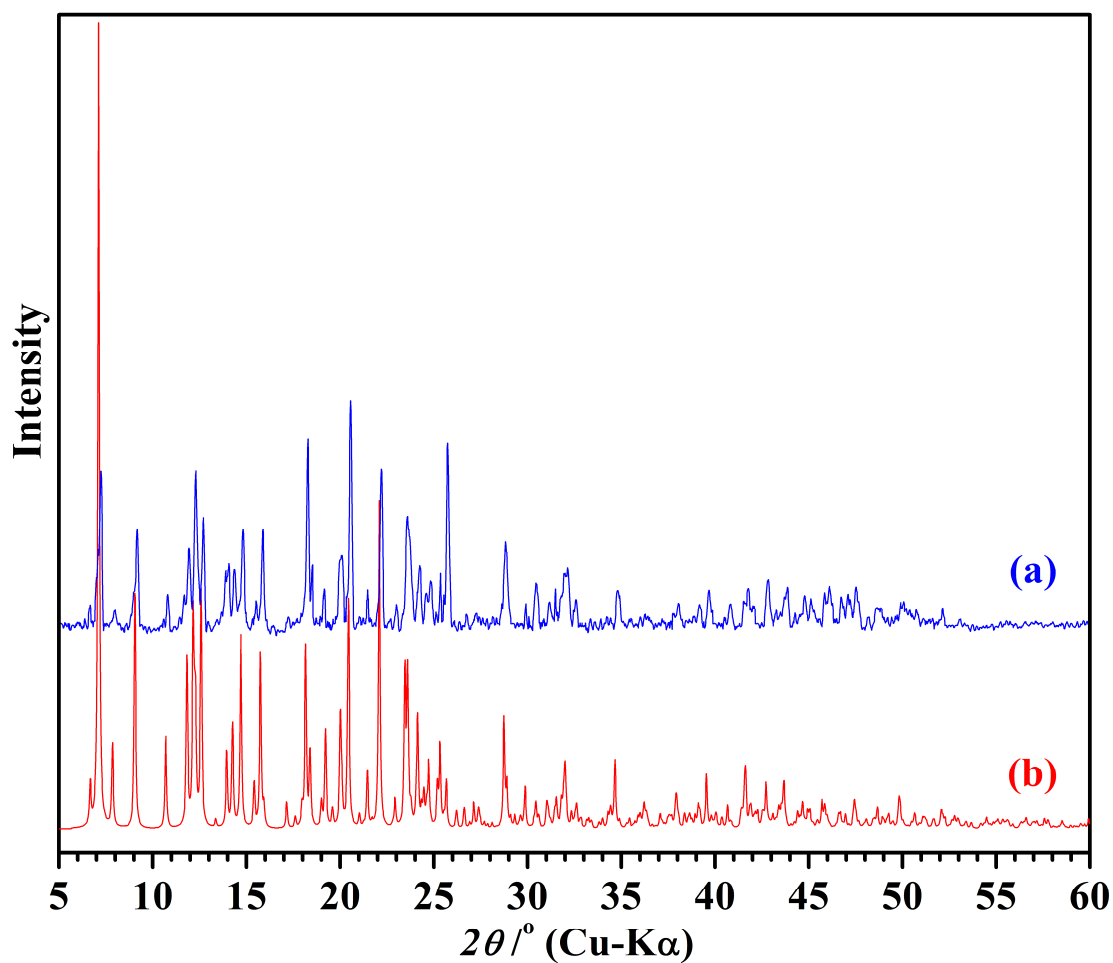


Fig. S10 The XRPD patterns for: (a) as-synthesized samples of **1** (blue), and (b) simulated one based on the single-crystal structure of **1** (red).

The peak positions of simulated and experimental XRPD patterns are in agreement with each other, indicating the good phase purity of compound **1**. The differences in intensity may be due to the preferred orientation of the crystalline powder sample.

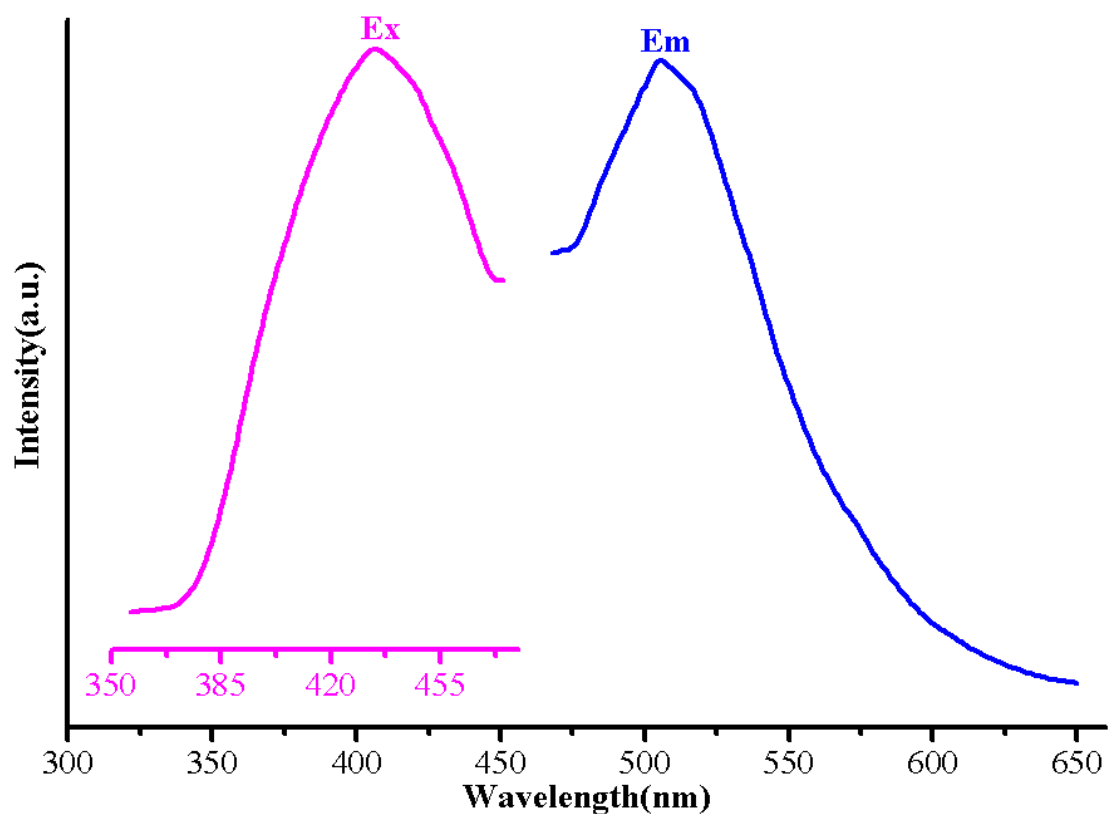


Fig. S11 Photoluminescent spectra of ppaH ligand in solid state at room temperature.

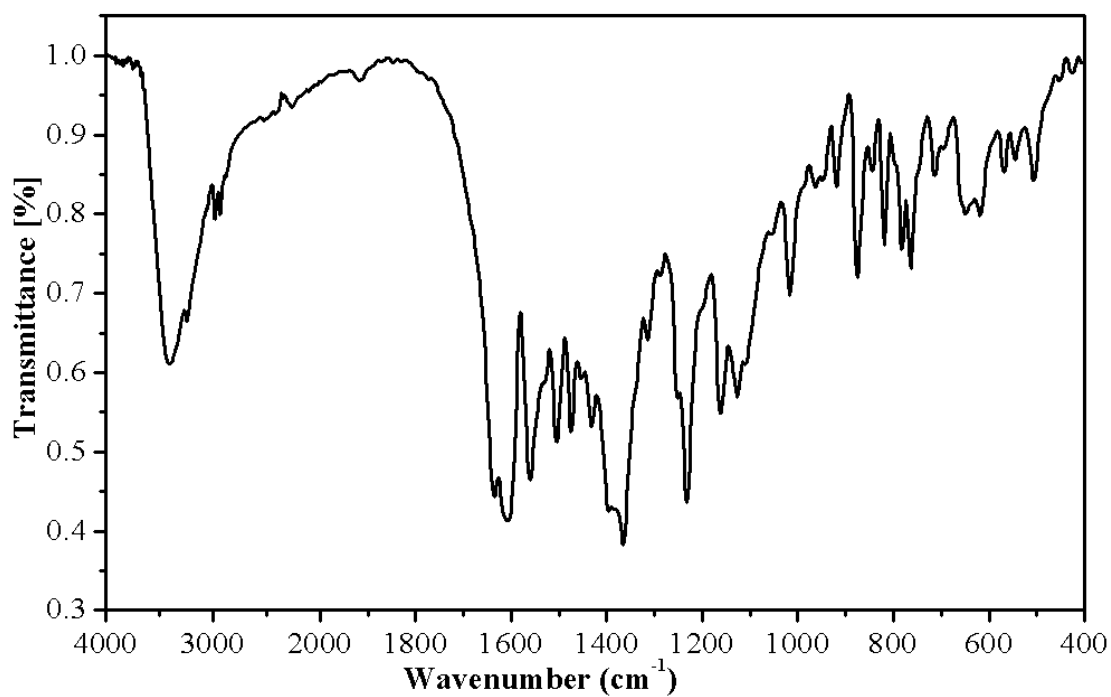


Fig. S12 The IR spectra for compound 1.